N sulfuric acid. This solution was poured into a 100-cc. flask which had reached the temperature of a water-bath at 100–101°. At the end of fifteen minutes, the cooled solution showed a rotation in a 4-dm. tube of −3.34°. A titration by the method of Cajori[10] showed a concentration of free arabinose equivalent to 0.365 g. in 50.0 cc. of solution indicating 81.7% hydrolysis and 0.1362 g. of unchanged arabinose diacetamide (specific rotation −8.9°). The rotation due to unchanged arabinose diacetamide is $(8.9 \times 4 \times 0.1362)/50$ or −0.11°. The 0.365 g. of free arabinose therefore contributes $-(3.34-0.11°)$ or −3.23° to the rotation of the mixture, corresponding to a specific rotation of −103.8° at 29°, a figure agreeing closely with the recorded equilibrium rotation of −104 to −105° for this sugar.

Hydrolysis of l-Threose Diacetamide.—A sample of 1.0519 g. of l-threose diacetamide was made up to 50 cc. with 0.100 N sulfuric acid at 20°. The solution was poured into a flask previously heated to 100° in a boiling water-bath. At intervals samples were taken and cooled to 20°; 5-cc. portions were measured out at that temperature and titrated by Cajori's method.[10,2]

The Equilibrium Rotation of l-Threose.—At the end of one hundred forty-four minutes of hydrolysis, the solution rotated +0.33° in a 2-dm. tube. The titration showed 0.453 g. of free tetrose per 50 cc. leaving 0.2216 g. of unchanged threose diacetamide. The rotation contributed by the latter is $(10.3 \times 2 \times 0.2216)/50$ or +0.09°, leaving −0.24° as the contribution of the free sugar. The specific rotation of the latter is $(-0.24 \times 50)/(2 \times 0.453)$ or +13.2°. This is considered to be in satisfactory agreement with the value of −12.5° obtained for d-threose.[2]

l-Threose Phenylosazone.—The hydrolyzate when treated with phenylhydrazine reagent,[2] deposited an osazone melting at 162° (corr.).

Summary

1. l-Xylose has been prepared by the oxidation of monobenzylidene d-sorbitol and diethylidene d-sorbitol with lead tetraacetate.

2. l-Xylose has been degraded by way of l-xylose oxime and tetraacetyl l-xylonic nitrile to l-threose diacetamide.

3. l-Threose diacetamide has been found to show a melting point of 165–167° (corr.) and a specific rotation in water of +10.3°, the latter value agreeing in magnitude with the rotation reported in the second paper of this series for d-threose diacetamide.

4. Partial hydrolysis of l-threose diacetamide with 0.1 N sulfuric acid and analysis of the resulting mixture of free sugar and diacetamide compound, along with polarimetric measurements, have permitted determination of the equilibrium specific rotation of l-threose in dilute acid solution as +13.2°. This value is in agreement with that announced for d-threose in the second paper of this series.

5. The foregoing method of determining the rotation of a sugar from its diacetamide derivative has been found accurate when applied to d-arabinose diacetamide.

6. Certain previously published rotations for d- and l-threose are considered to be erroneous.

7. Several new derivatives of d-threose, l-threose, d-lyxose and d-arabinose are reported.
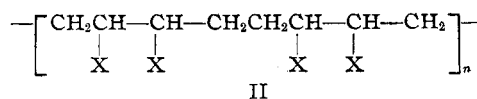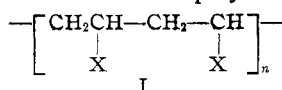
Cambridge, Massachusetts
Buenos Aires, Argentine

[Contribution from the Chemical Laboratory of the University of Illinois]

The Structure of Vinyl Polymers: the Polymer from Methyl Vinyl Ketone

By C. S. Marvel and Charles L. Levesque[1]

The structures of the products obtained by the peroxide catalyzed polymerization of various vinyl compounds of the type CH_2=CHX (X= halogen, $-\overset{\text{O}}{\underset{\|}{C}}-H$, $-\overset{\text{O}}{\underset{\|}{C}}-R$, $-\overset{\text{O}}{\underset{\|}{C}}-OR$, $-\overset{\text{O}}{\underset{\|}{O}}CR$, C_6H_5, etc.) have been considered by many investigators. Obviously there are three ways in which units of the vinyl type may combine to form a long chain molecule. The units may join in a "head to tail" fashion to produce a linear polymer of type I;

$$-\left[\underset{X}{CH_2CH}-CH_2-\underset{X}{CH} \right]_n-$$

I

$$-\left[\underset{X}{CH_2CH}-\underset{X}{CH}-CH_2CH_2\underset{X}{CH}-\underset{X}{CH}-CH_2 \right]_n-$$

II

in a "head to head, tail to tail" fashion to give a linear polymer of type II; or in a random fashion to give a linear polymer in which some of the substituents are on adjacent carbons and some are in the 1,3-positions with respect to each other.

In some of the earlier work on this type of polymer Ostromysslenski[2] presented evidence which he felt proved that polyvinyl bromide was identical with the perbromide of polybutadiene
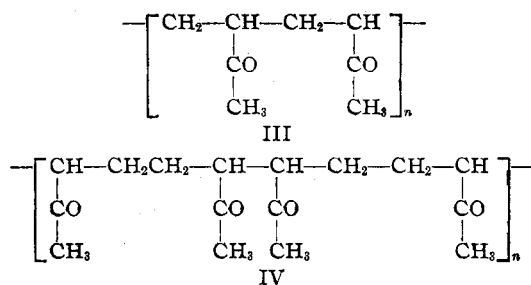
(1) Cramer Foundation Fellow from Dartmouth College.

(2) Ostromysslenski, *J. Russ. Phys. Chem. Soc.*, **44**, 240 (1912); *Chem. Zent.*, **83**, I, 1982 (1912).

and hence had the 1,2-dihalide structure (type II). However, Harries[3] and later Staudinger and his co-workers[4] have cast considerable doubt on these results. Moreover, the work of Staudinger and Steinhofer[5] on polystyrene has indicated that this linear polymer has the structure indicated by formula I (X = C_6H_5). This structure has been questioned by Midgley, Henne and Leicester,[6] who definitely favor the type II structure for polystyrene.

Recent work from this Laboratory[7] on the structures of polysulfones produced by the addition of sulfur dioxide to olefins by a polymerization reaction catalyzed by peroxides has shown that these compounds are unquestionably of the "head to head, tail to tail" type (II). In view of these conflicting results, it has seemed worthwhile to try to find definite chemical evidence to support the structures of several of the commoner vinyl type polymers.

The polymer from methyl vinyl ketone is admirably suited to the study of this problem since the "head to tail" type (III) of polymeric structure is that of a 1,5-diketone whereas the "head to head, tail to tail" type of polymeric structure is

$$-\left[CH_2-CH-CH_2-CH \atop \underset{CH_3}{\overset{|}{CO}} \underset{CH_3}{\overset{|}{CO}} \right]_n-$$

III

$$-\left[CH-CH_2CH_2-CH-CH-CH_2-CH_2-CH \atop \underset{CH_3}{\overset{|}{CO}} \underset{CH_3}{\overset{|}{CO}} \underset{CH_3}{\overset{|}{CO}} \underset{CH_3}{\overset{|}{CO}} \right]_n-$$

IV

that of a 1,4-diketone (IV). These types of ketones have quite different chemical reactions and hence it should be possible to distinguish between the two possible structures for the polymer itself.

The polymer used in our experiments was prepared by warming methyl vinyl ketone containing a little benzoyl peroxide. The polymer was a faintly yellow, clear, tough mass which was soluble in many of the common organic solvents; hence, it was undoubtedly a linear polymer of fairly low molecular weight.

(3) Harries, Ann., 395, 216 (1913).

(4) Staudinger, Brunner and Feisst, Helv. Chim. Acta, 13, 805 (1930).
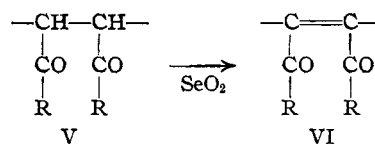
(5) Staudinger and Steinhofer, Ann., 517, 35 (1935).

(6) Midgley, Henne and Leicester, THIS JOURNAL, 58, 1961 (1936).

(7) Hunt and Marvel, ibid., 57, 1691 (1935); Glavis, Ryden and Marvel, ibid., 59, 707 (1937).

Treatment of a dilute dioxane or pyridine solution of this polymer with anhydrous zinc chloride at 50–60° did not change its properties in any appreciable degree. When phosphorus pentoxide was substituted for the zinc chloride in this reaction mixture, a highly colored, insoluble and infusible substance was produced. This product was undoubtedly formed by some reaction which produced cross linking between the polymeric chains.

The conversion of 1,4-diketones to furan derivatives by the action of zinc chloride or phosphorus pentoxide is a well-known reaction[8] and the fact that the polymer of methyl vinyl ketone does not dehydrate with these reagents is strong evidence against the 1,4-diketone structure (IV) for this polymer.

Selenium dioxide usually oxidizes 1,4-diketones (V) to the diacylethylenes[9] (VI). When the

$$\underset{V}{-CH-CH- \atop \underset{R}{\overset{|}{CO}} \, \underset{R}{\overset{|}{CO}}} \quad \xrightarrow{SeO_2} \quad \underset{VI}{-C==C- \atop \underset{R}{\overset{|}{CO}} \, \underset{R}{\overset{|}{CO}}}$$

polymer of methyl vinyl ketone was treated with selenium dioxide, oxidation occurred but an analysis of the oxidation products showed that oxygen had been added to the molecule. This indicates that some of the methyl ketone groups may have been converted to hydrated glyoxal groups, a reaction which would be expected with a polymethyl ketone in which the ketone groups are farther apart than the 1,4-positions.[10]

Since both of these reactions indicated the 1,5-diketone rather than the 1,4-diketone structure, an attempt was made to apply Knoevenagel's pyridine synthesis[11] from a 1,5-diketone and hydroxylamine to the polymeric ketone. The polymeric ketone was readily converted to the oxime (VII) which proved to be soluble in both acids and alkalies. No evidence of the formation of a polypyridine derivative (VIII) was obtained.
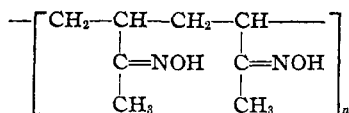
During the combustion analysis of a sample of the polyketone it was noted that water was given off readily when the polymer was heated. Accordingly attempts were made to pyrolyze the polymer in a nitrogen atmosphere at 270–360°. Water distilled first and was obtained to the ex-
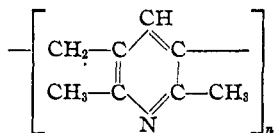
(8) Dietrich and Paal, Ber., 20, 1085 (1887).

(9) Astin, Moulds and Riley, J. Chem. Soc., 902 (1935); Armstrong and Robinson, ibid., 1650 (1934).

(10) Riley, Morley and Friend, ibid., 1877 (1932).

(11) Knoevenagel and others, Ann., 281, 25 (1894).

$$-\left[\begin{array}{c}CH_2-CH-CH_2-CH- \\ \ \ \ \ \ \ | \ \ \ \ \ \ \ \ \ | \\ \ \ \ \ \ \ C=NOH \ \ \ C=NOH \\ \ \ \ \ \ \ | \ \ \ \ \ \ \ \ \ | \\ \ \ \ \ \ \ CH_3 \ \ \ \ \ \ \ CH_3\end{array}\right]_n$$

VII

$$-\left[\begin{array}{c} \ \ \ \ \ \ \ \ \ CH \\ CH_2-C \diagup \diagdown C- \\ \ \ \ \ \ \ || \ \ \ \ \ || \\ CH_3-C \diagdown \diagup C-CH_3 \\ \ \ \ \ \ \ \ \ \ N \end{array}\right]_n$$

VIII

tent of 20–22% of the weight of the polymer. This is essentially equivalent to one molecule of water for each unit of methyl vinyl ketone in the polymer. After the water ceased to distil rapidly the temperature of the heating bath was raised and the residual polymer was "cracked." Volatile organic material corresponding to about 16–18% of the weight of the polymer was obtained.

The organic products of pyrolysis were most complex. Only the lowest boiling constituent was isolated and it was identified as 3-methyl-Δ^2-cyclohexenone (IX). The other fractions boiled

$$\begin{array}{c} \ \ \ \ \ \ \diagup CH_2 \\ \ \ \ \ CH_2 \diagdown CH_2 \\ CH_3-C \ \ \ \ \diagup C=O \\ \ \ \ \ \ \ \diagdown CH \end{array}$$
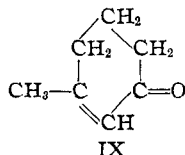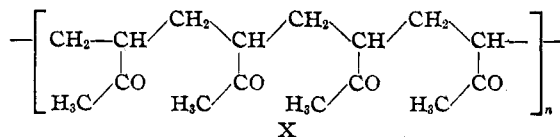
IX

over a wide range and varied from a light yellow liquid to an orange gel. The lower boiling fractions gave tests for ketone groups with 2,4-dinitrophenylhydrazine. Heating these portions with selenium gave alkali-soluble products which had the characteristic phenol odor. These products must therefore be six-membered ring ketones which can be dehydrogenated to phenols.
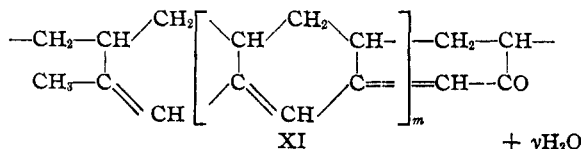
When volatile liquid products ceased to come over in the distillate with the bath at 360°, the pyrolysis was stopped. The non-volatile material was a clear, red, glassy solid which was fusible and somewhat soluble in acetone. Thus, the pyrolysis reaction did not cause cross-linking of the chains or production of a polymer of much higher molecular weight. This residue contained some oxygen.

All of the results obtained in the pyrolysis experiments can be readily accounted for on the basis of structure III for the polymer of methyl vinyl ketone. The loss of most of the oxygen as water, the formation of six-membered carbon rings containing carbonyl groups and the formation of a residue poor in oxygen which is still a

soluble polymer are the results to be expected by heating a polymeric methyl ketone with the carbonyl groups in the 1,5-position with respect to each other. The following formulas make clear the change which occurs as the major reaction. The residual polymer probably is the condensed ring system shown in formula XI.

$$-\left[\begin{array}{c}CH_2-CH \diagup CH_2 \diagdown CH \diagup CH_2 \diagdown CH \diagup CH_2 \diagdown CH- \\ \ \ \ \ \ \ | \ \ \ \ \ \diagdown CO \ \ \ \ \ \ \diagdown CO \ \ \ \ \ \diagdown CO \ \ \ \ \ \diagdown CO \\ \ \ \ \ \ H_3C \diagup \ \ \ \ \ H_3C \diagup \ \ \ \ H_3C \diagup \ \ \ \ H_3C \diagup \end{array}\right]_n$$

X

$$-CH_2-CH \diagup CH_2 \left[\begin{array}{c} \diagdown CH \diagup CH_2 \diagdown CH- \\ \ \ \ \ \ \ \ \ \diagup C \diagdown \ \ \ \ \ \ \ \ C== \\ \ \ \ \ \ \ \diagdown CH \diagup \end{array}\right]_m -CH_2-CH- \\ CH_3-C \diagdown \ =CH-CO \\ \ \ \ \ \ \ \ \diagdown CH$$

XI $+ yH_2O$

The very small quantity of 3-methyl-Δ^2-cyclohexenone which was obtained is not surprising since the molecular structure is such that formation of the condensed ring system is favored; only the small end portions which are broken off before the loss of water is complete can yield the ketonic compounds which were present in the distillate from the pyrolysis.

It is especially significant that the 1,4-diketone structure (IV) for the polymeric ketone cannot account for any of the pyrolysis products. It is possible that a random arrangement in which most of the units are combined to give the 1,5-diketone structure (III) might explain the results. But judging from the fact that the loss of water on pyrolysis corresponds closely to one mole per unit of ketone, essentially all of the units must be arranged in the same manner and the random structure seems unlikely.

Experimental

Preparation of the Polymer of Methyl Vinyl Ketone.[12]— About 0.5% by weight of benzoyl peroxide was added to freshly distilled methyl vinyl ketone and the solution thus obtained was heated at 50–60° for five hours. This treatment produced a faintly yellow, clear tough mass which was soluble in acetone, acetic acid, acetic anhydride, dioxane, pyridine, and hot cellosolve but insoluble in water, alcohol, ether and benzene. The sample for analysis was dried under reduced pressure at 80° over phosphorus pentoxide.

Anal. Calcd. for $(C_4H_6O)_n$: C, 68.5; H, 8.63. Found: C, 67.89, 68.00; H, 8.63, 8.54.

(12) The preparation of a polymeric compound from methyl vinyl ketone has been described in the following patents: U. S. Patent 1,755,099, *C. A.*, **24**, 2905 (1930); German Patent 555,859, *C. A.*, **26**, 6165 (1932); U. S. Patent 1,896,161, *C. A.*, **27**, 2458 (1933); U. S. Patent 2,005,295, *C. A.*, **29**, 5203 (1935).

Attempted Dehydration of the Polymer.—To a solution of 0.82 g. of the polyketone in 23 cc. of dioxane was added 10 g. of anhydrous zinc chloride, and the solution was heated to 56° and stirred for three days at that temperature. The solution was filtered and the polymer was precipitated by the addition of water. The product isolated weighed 0.4 g. and had properties very much like the original polymer. Analysis indicated a little water might have been removed but the variations in carbon and hydrogen content were not enough to be significant.

Anal. Calcd. for the polyketone $(C_4H_6O)_n$: C, 68.5; H, 8.63. Calcd. for the polyfuran $(C_8H_{10}O)_n$: C, 78.62; H, 8.19. Found: C, 70.10; H, 8.88.

A similar experiment in which pyridine was used as the solvent in place of dioxane gave essentially the same result.

Oxidation of the Polyketone with Selenium Dioxide.— To a solution of 1.55 g. of the polymeric ketone in 400 cc. of dioxane was added 0.65 g. of selenium dioxide and the mixture was boiled under a reflux condenser for about sixteen hours. The mixture was filtered and the filtrate concentrated to 150 cc. The colloidal selenium was removed by saturating the solution with hydrogen sulfide and filtering it through a layer of decolorizing carbon. This filtrate was evaporated to about 5 cc. and water was added to precipitate the polymer. The precipitate was collected on a filter. The yield was 0.71 g. of a tough yellow solid. The product was dried under reduced pressure at 80° over phosphorus pentoxide and analyzed.

Anal. Calcd. for

$$\left[\begin{array}{cc} CH_2C{=}CCH_2 \\ | \quad\quad | \\ CO \quad CO \\ | \quad\quad | \\ CH_3 \quad CH_3 \end{array}\right]_n$$

C, 69.5; H, 7.24.

Calcd. for

$$\left[\begin{array}{c} CH_2CH{-} \\ | \\ CO \\ | \cdot H_2O \\ CO \\ | \\ H \end{array}\right]_n$$

C, 47.8; H, 5.94.

Found: C, 58.59, 59.19; H, 7.40, 7.83.

These two analyses are of products from different experiments.

Oxime of the Polyketone.—A mixture of 200 cc. of 95% alcohol, 200 cc. of dioxane and 5.1 g. of anhydrous sodium acetate was placed in a three-necked flask fitted with a stirrer, reflux condenser and two dropping funnels. The solution was heated to boiling and solutions of 4.2 g. of hydroxylamine hydrochloride in 200 cc. of 95% alcohol and 4.2 g. of polyketone in 150 cc. of dioxane were added dropwise at equivalent rates. The mixture first became milky in appearance but cleared up soon after the addition of all the reagent was complete. A white solid coagulated and was collected on a filter, washed thoroughly with water and dried. The yield was 4.0 g. of a white powdery substance soluble in strong acids or bases but insoluble in water.

Anal. Calcd. for $(C_4H_7ON)_n$: N, 16.46. Found: N, 16.27, 16.41.

Pyrolysis of the Polyketone.—Thirty-seven grams of methyl vinyl ketone was polymerized in a Claisen flask. The flask was then fitted with a receiver connected with an acetone–dry ice trap to collect any highly volatile

material and a small capillary tube to admit nitrogen. The system was evacuated to about 3 mm. pressure and while a very slow stream of nitrogen was admitted to exclude all air, the flask was quickly heated to 270°. The polymer melted and water began to distil rapidly. The water appeared as ice in the acetone–dry ice trap. After heating at 270° for about three hours, the mixture seemed to have ceased decomposing. During this time some yellowish liquid had distilled. The undistilled residue in the flask was a dark red liquid. The heating bath temperature was then raised at the rate of about 10° per hour until the temperature reached 360°. During this time little water came over and the material that did distil was noticeably more viscous. At the end the distillate was a semi-solid orange gel which clogged the side-arm. The pyrolysis was stopped at this stage. The total heating time was about fifteen hours.

From the dry ice–acetone trap 7.5 g. of water was obtained. It was identified by boiling point and refractive index.

The residue which did not distil contained 19.7 g. of material which on cooling set to a hard, clear, red, glassy solid. It was slightly soluble in acetone.

Anal. C, 85.94; H, 7.49.

The volatile organic material weighed 7.7 g. It was a viscous dark yellow liquid. Two fractional distillations gave the following fractions: Fraction I, 0.56 g. of a pale yellow liquid, b. p. 68–71° at 3 mm., $n^{20}D$ 1.4912, d^{20}_4 0.9704; Fraction II, 0.96 g. of a yellow liquid, b. p. 117–122° at 3.5 mm., $n^{20}D$ 1.5193, d^{20}_4 1.0569; Fraction III, 0.72 g. of a dark yellow liquid, b. p. 129–134° at 3.5 mm., $n^{20}D$ 1.5410; Fraction IV, 0.48 g. of an orange-yellow liquid, b. p. 162–184° at 3 mm., $n^{20}D$ 1.5620; Fraction V, 1.2 g. of a viscous yellow liquid, b. p. 184–205° at 3 mm., $n^{20}D$ 1.5718; Fraction VI, a thick viscous red residue.

A second pyrolysis experiment using 32 g. of polyketone and heating at 260–330° for twenty-four hours gave 7 g. of water, 5.2 g. of distillate and 19.2 g. of glassy residue.

Identification of Fraction I.—Analysis of fraction I indicated that it was a methylcyclohexenone.

Anal. Calcd. for $C_7H_{10}O$: C, 76.4; H, 9.16. Found: C, 76.79; H, 8.98.

The physical properties also checked closely with those of the known 3-methyl-Δ^2-cyclohexenone.[13]

The 2,4-dinitrophenylhydrazone of fraction I was prepared by the method of Allen[14] and after five recrystallizations from alcohol melted at 166.7–169.8°.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: N, 19.3. Found: N, 19.0.

The melting point of a mixture of this sample with a known specimen of the 2,4-dinitrophenylhydrazone of 3-methyl-Δ^2-cyclohexenone was 168–171.8°, whereas the authentic specimen itself melted at 172.5–173°.

3-Methyl-Δ^2-cyclohexenone.—A sample of this ketone was synthesized for comparison with fraction I. To a solution of 5 g. of sodium in 200 cc. of absolute alcohol was added 34 cc. of ethyl acetoacetate and then 18 cc. of methyl vinyl ketone in 20 cc. of absolute alcohol. The

(13) Knoevenagel, *Ann.*, **297**, 182 (1897); Rabe, *Ber.*, **40**, 2482 (1907); Harries, *ibid.*, **47**, 790 (1914).

(14) Allen, THIS JOURNAL, **52**, 2955 (1930).

reaction mixture was allowed to stand at room temperature for about forty hours. Most of the alcohol was removed under reduced pressure and the residue was warmed at 50–60° for four hours with 150 cc. of 5% sodium hydroxide solution. This solution was cooled and acidified with dilute sulfuric acid. The organic material was extracted with ether, dried over anhydrous sodium sulfate and distilled.

The yield of 3-methyl-Δ^2-cyclohexenone was 3 g. (12.5%), b. p. 86–88° at 14 mm.; n^{20}D 1.4940.

The 2,4-dinitrophenylhydrazone after three crystallizations from alcohol melted at 172.5–173°.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$: N, 19.30. Found: N, 19.31.

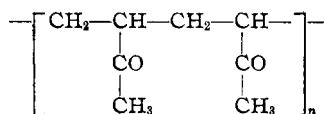The semicarbazone was also prepared and it melted at 201–201.2° which agrees with the melting point previously reported.[13]

Some Reactions of Other Fractions of the Distillate from Pyrolysis.—Fraction II from the pyrolysis mixture reacted with 2,4-dinitrophenylhydrazine to give a product melting at 138–146° but it could not be purified to give a chemical individual.

Fraction III was heated with selenium to 300–320° for seven hours. After cooling the melt was extracted with 10% sodium hydroxide solution and the solution was filtered. On acidifying the filtrate a light colored, ethersoluble powder with a marked phenolic odor was obtained. The powder did not melt sharply and no pure products were isolated.

Summary

Evidence has been presented to show that the polymer of methyl vinyl ketone has the "head to tail" structure

$$-\left[\begin{array}{c} CH_2-CH-CH_2-CH- \\ \qquad | \qquad\qquad | \\ \qquad CO \qquad\quad CO \\ \qquad | \qquad\qquad | \\ \qquad CH_3 \qquad\; CH_3 \end{array} \right]_n-$$

Condensations by Sodium. XI. Trimethoxytrixenylcarbinol and Comparisons of Colors of Some Carbonium Salts in this Series

BY AVERY A. MORTON AND WILLIAM S. EMERSON

Tris-[4′-methoxytrixenyl]-carbinol has now been prepared by the reactions represented in the equation

$$3CH_3OC_2H_4C_2H_4Br + 6Na + (C_2H_5)_2CO_3 \longrightarrow$$
$$(CH_3OC_6H_4C_6H_4)_3CONa + 3NaCl + 2NaOC_2H_5$$
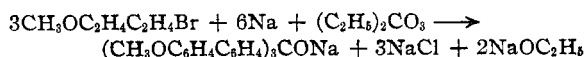
Besides demonstrating the effectiveness of sodium as an agent in the preparation of large size triarylcarbinols, our purpose[1] was to observe qualitatively the effect on color, and therefore presumably on basicity, of introducing an additional phenyl group between the functioning and influencing groups. We are now able to state that the order of the effect of substituents as observed in the triphenylmethane series by Baeyer and Villiger[2] and by Ziegler and Boye,[3] namely, MeO > CH₃ > H, is preserved in the trixenylmethane series and that the parent member of this series, trixenylcarbinol, is a far stronger color producing substance than the corresponding carbinol of the triphenylmethane series. In general the basic characters of the two series of carbinols are parallel, the introduction of the methoxy group causing a considerable increase in the basicity of both.[4]

The Hardy[5] color analyzer is particularly well adapted to measurements of this kind. This instrument measures the transmission T, of light through solutions at definite wave lengths, 100% T meaning that the transmission is the same as that of a colorless blank solution and 0% indicating that the color is so intense that no light of that wave length passes. The amount of color is proportional to log $1/T$. Results are mechanically plotted, a typical set of curves being shown in Fig. 1. All of the data are summarized in Table I. Visually at the very low acid concentration of 0.000667 triphenylcarbinol showed no color, trixenylcarbinol was a faint pink, trimethyltrixenylcarbinol was a strong purple, and trimethoxytrixenylcarbinol was an intense blue. The trimethoxy derivative, indeed, becomes colored at or near the neutral point in cold glacial acetic acid.

We are particularly grateful to Professor Hardy

(1) See Morton and Emerson, THIS JOURNAL, **59**, 1947 (1937).

(2) Baeyer and Villiger, *Ber.*, **35**, 1189 (1902).

(3) Ziegler and Boye, *Ann.*, **458**, 229 (1927).

(4) See Kolthoff, THIS JOURNAL, **49**, 1218 (1927); Lund, *ibid.*, 1346, for the effect of introducing methoxy groups in triphenylcarbinol.

(5) Hardy, *J. Optical Soc. Am.*, **18**, 96 (1929); **25**, 305 (1935).